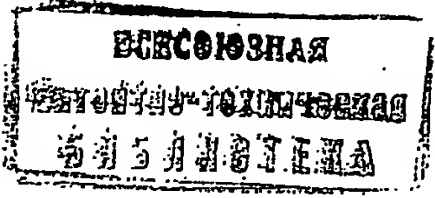




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> FIRE EXTINGUISHING METHODS AND BLENDS UTILIZING HYDROFLUOROCARBONS  <b>(57) Abstract</b>  Highly fluorinated, saturated, C <sub>2</sub> and C <sub>3</sub> hydrofluorocarbons are efficient, economical, non-ozone-depleting fire extinguishing agents used alone or in blends with other fire extinguishing agents in total flooding and portable systems.		

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- 1 -

FIRE EXTINGUISHING METHODS AND BLENDS  
UTILIZING HYDROFLUOROCARBONS

CROSS-REFERENCE

This application is a continuation-in-part of 5 applicants' co-pending United States patent application, Serial No. 396,841, filed August 21, 1989.

BACKGROUND OF THE INVENTION

Field of the Invention.

This invention relates to fire extinguishing 10 methods and blends utilizing higher fluorinated C<sub>2</sub> and C<sub>3</sub> saturated hydrofluorocarbons.

Description of the Prior Art.

The use of certain bromine, chlorine and iodine-containing halogenated chemical agents for the 15 extinguishment of fires is common. These agents are in general thought to be effective due to their interference with the normal chain reactions responsible for flame propagation. The most widely accepted mechanism for flame suppression is the radical trap mechanism proposed 20 by Fryburg in Review of Literature Pertinent to Fire Extinguishing Agents and to Basic Mechanisms Involved in Their Action, NACA-TN 2102 (1950). The finding that the effectiveness of the halogens are on a molar basis in the order Cl<Br<I supports the radical trap mechanism, as 25 reported by Malcom in Vaporizing Fire Extinguishing Agents, Report 117, Dept. of Army Engineering Research and Development Laboratories, Fort Bevoir, VA, 1950 (Project- 8-76-04-003). It is thus generally accepted that compounds containing the halogens Cl, Br and I act 30 by interfering with free radical or ionic species in the flame and that the effectiveness of these halogens is in the order I>Br>Cl.

In contrast, hydrofluorocarbons (i.e., compounds containing only C, H and F atoms) have not 35 heretofore been recognized to display any chemical action in the suppression of combustion. Thus, it is generally

- 2 -

thought that to be effective as a fire extinguishing agent, a compound must contain Cl, Br or I.

The use of iodine-containing compounds as fire extinguishing agents has been avoided primarily due to the expense of their manufacture or due to toxicity considerations. The three fire extinguishing agents presently in common use are all bromine-containing compounds, Halon 1301 ( $\text{CF}_3\text{Br}$ ), Halon 1211 ( $\text{CF}_2\text{BrCl}$ ) and Halon 2402 ( $\text{CF}_2\text{BrCF}_2\text{Br}$ ). The effectiveness of these three volatile bromine-containing compounds in extinguishing fires has been described in U.S. Patent 4,014,799 to Owens. Although not employed commercially, certain chlorine-containing compounds are also known to be effective extinguishing agents, for example Halon 251 ( $\text{CF}_3\text{CF}_2\text{Cl}$ ) as described by Larsen in U.S. Patent 3,844,354.

Although the above named bromine-containing Halons are effective fire fighting agents, those agents containing bromine or chlorine are asserted by some to be capable of the destruction of the earth's protective ozone layer. Also, because the agents contain no hydrogen atoms which would permit their destruction in the troposphere, the agents may also contribute to the greenhouse warming effect.

It is therefore an object of this invention to provide a method for extinguishing fires that extinguishes fires as rapidly and effectively as the techniques employing presently used Halon agents while avoiding the above-named drawbacks.

It is a further object of this invention to provide an agent for the use in a method of the character described that is efficient, economical to manufacture, and environmentally safe with regard to ozone depletion and greenhouse warming effects.

It is a still further object of this invention to provide blends of hydrofluorocarbons and other fire extinguishing agents that are effective and

- 3 -

environmentally safe.

- 4 -

SUMMARY OF THE INVENTION

The foregoing and other objects, advantages and features of the present invention may be achieved by employing saturated, higher fluorinated hydrofluorocarbons and blends thereof with other agents as fire extinguishants for use in fire extinguishing methods and apparatus. More particularly, the method of this invention involves introducing to a fire a saturated  $C_2$  or  $C_3$  higher fluorinated hydrofluorocarbon in a fire extinguishing concentration and maintaining such concentration until the fire is extinguished. Saturated higher fluorinated hydrofluorocarbons of this invention include compounds of the formula  $C_xH_yF_z$ , where x is 2 or 3; y is 1 or 2; and z is 5, 6 or 7; where y is 1 and z is 5 when x is 2 and where z is 6 or 7 when x is 3. Specific hydrofluorocarbons useful in accordance with this invention include heptafluoropropane ( $CF_3CHF_2$ ), 1,1,1,3,3,3-hexafluoropropane ( $CF_3CH_2CF_3$ ), 1,1,1,2,3,3-hexafluoropropane ( $CF_3CHFCHF_2$ ) and pentafluoroethane ( $CF_3CHF_2$ ). These hydrofluorocarbons may be used alone, in admixture with each other or as blends with other fire extinguishing agents. Generally, the agents of this invention are employed at concentrations lying in the range of about 3 to 15%, preferably 5 to 10%, on a v/v basis.

- 5 -

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, saturated higher fluorinated  $C_2$  and  $C_3$  hydrofluorocarbons have been found to be effective fire extinguishants at 5 concentrations safe for use. However, because such hydrofluorocarbons contain no bromine or chlorine, they have an ozone depletion potential of zero. Furthermore, since the compounds contain hydrogen atoms, they are susceptible to breakdown in the lower atmosphere and 10 hence do not pose a threat as greenhouse warming gasses.

Specific hydrofluorocarbons useful in accordance with this invention are compounds of the formula  $C_xH_yF_z$ , where  $x$  is 2 or 3;  $y$  is 1 or 2; and  $z$  is 5, 6 or 7; where  $y$  is 1 and  $z$  is 5 when  $x$  is 2; and where 15  $z$  is 6 or 7 when  $x$  is 3. Specific hydrofluorocarbons useful in accordance with this invention include heptafluoropropane ( $CF_3CHF_2$ ), 1,1,1,3,3,3-hexafluoropropane ( $CF_3CH_2CF_3$ ), 1,1,1,2,3,3-hexafluoropropane ( $CF_3CHFCHF_2$ ), and pentafluoroethane ( $CF_3CHF_2$ ).

20 These compounds may be used alone or in admixture with each other or in blends with other fire extinguishing agents. Among the other agents with which the hydrofluorocarbons of this invention may be blended are chlorine and/or bromine containing compounds such as 25 Halon 1301 ( $CF_3Br$ ), Halon 1211 ( $CF_2BrCl$ ), Halon 2402 ( $CF_2BrCF_2Br$ ), Halon 251 ( $CF_3CF_2Cl$ ) and  $CF_3CHFBr$ . Mixtures of heptafluoropropane and Halon 1201 ( $CF_2HBr$ ) are especially preferred because the compounds have similar vapor pressures over a wide range of temperatures and 30 therefore the composition of the mixture remains relatively constant during discharge or other application.

Where the hydrofluorocarbons of this invention are employed in blends, they are desirably present at a 35 level of at least about 10 percent by weight of the blend. The hydrofluorocarbons are preferably employed at higher levels in such blends so as to minimize the

- 6 -

adverse environmental effects of chlorine and bromine containing agents.

The hydrofluorocarbon compounds used in accordance with this invention are non-toxic and are economical to manufacture. For example, heptafluoropropane may be conveniently produced via the reaction of commercially available hexafluoropropene ( $\text{CF}_3\text{CF}=\text{CF}_2$ ) with anhydrous HF as described in U.K. Patent 902,590. Similarly, 1,1,1,3,3,3-hexafluoropropane may be synthesized by reacting anhydrous HF with pentafluoropropene ( $\text{CF}_3\text{CH}=\text{CF}_2$ ).

1,1,1,2,3,3-hexafluoropropane may be obtained by hydrogenation of hexafluoropropene ( $\text{CF}_3\text{CF}=\text{CF}_2$ ).

Pentafluoroethane may be obtained by the addition of hydrofluoric acid to tetrafluoroethylene ( $\text{CF}_2=\text{CF}_2$ ).

The saturated highly fluorinated  $\text{C}_2$  and  $\text{C}_3$  hydrofluorocarbons of this invention may be effectively employed at substantially any minimum concentrations at which fire may be extinguished, the exact minimum level being dependent on the particular combustible material, the particular hydrofluorocarbon and the combustion conditions. In general, however, best results are achieved where the hydrofluorocarbons or mixtures and blends thereof are employed at a level of at least about 3% (v/v). Where hydrofluorocarbons alone are employed, best results are achieved with agent levels of at least about 5% (v/v). Likewise, the maximum amount to be employed will be governed by matters of economics and potential toxicity to living things. About 15% (v/v) provides a convenient maximum concentration for use of hydrofluorocarbons and mixtures and blends thereof in occupied areas. Concentrations above 15 % (v/v) may be employed in unoccupied areas, with the exact level being determined by the the particular combustible material, the hydrofluorocarbon (or mixture or blend thereof) chosen and the conditions of combustion. The preferred concentration of the hydrofluorocarbon agents, mixtures



- 7 -

and blends in accordance with this invention lies in the range of about 5 to 10% (v/v).

Hydrofluorocarbons may be applied using conventional application techniques and methods used for 5 Halons such as Halon 1301 and Halon 1211. Thus, these agents may be used in a total flooding fire extinguishing system in which the agent is introduced to an enclosed region (e.g., a room or other enclosure) surrounding a fire at a concentration sufficient to extinguish the 10 fire. In accordance with a total flooding system apparatus, equipment or even rooms or enclosures may be provided with a source of agent and appropriate piping, valves, and controls so as automatically and/or manually to be introduced at appropriate concentrations in the 15 event that fire should break out. Thus, as is known to those skilled in the art, the fire extinguishant may be pressurized with nitrogen or other inert gas at up to about 600 psig at ambient conditions.

Alternatively, the hydrofluorocarbon agents may 20 be applied to a fire through the use of conventional portable fire extinguishing equipment. It is usual to increase the pressure in portable fire extinguishers with nitrogen or other inert gasses in order to insure that the agent is completely expelled from the the 25 extinguisher. Hydrofluorocarbon containing systems in accordance with this invention may be conveniently pressurized at any desirable pressure up to about 600 psig at ambient conditions.

Practice of the present invention is 30 illustrated by the following Examples, which are presented for purposes of illustration but not of limitation.

#### EXAMPLE 1

A 28.3 cubic litre test enclosure was 35 constructed for static flame extinguishment tests (total flooding). The enclosure was equipped with a Plexiglas viewport and an inlet at the top for the agent to be

- 8 -

tested and an inlet near the bottom to admit air. To test the agent, a 90 x 50 mm glass dish was placed in the center of the enclosure and filled with 10 grams of cigarette lighter fluid available under the trademark 5 RONSONOL. The fuel was ignited and allowed a 15 second preburn before introduction of the agent. During the preburn, air was admitted to the enclosure through the lower inlet. After 15 seconds, the air inlet was closed and the fire extinguishing agent was admitted to the 10 enclosure. A predetermined amount of agent was delivered sufficient to provide 6.6% v/v concentration of the agent. The extinguishment time was measured as the time between admitting the agent and extinguishment of the flame. Average extinguishment times for a 6.6% v/v 15 concentration of heptafluoropropane, Halon 1301, Halon 1211 and  $\text{CF}_3\text{CHFBr}$  are given in Table 1.

EXAMPLE 2

The experimental procedure of Example 1 was carried out employing heptane as the fuel. The average 20 extinguishment times for 6.6% v/v of the same agents are also given in Table 1.

Table 1

Extinguishment Time (seconds) for 6.6 % v/v Agent

25	Agent	Lighter fluid	n-Heptane
	$\text{CF}_3\text{CHF}\text{CF}_3$	1.6	1.6
	$\text{CF}_3\text{Br}$ (Halon 1301)	0.8	1.4
30	$\text{CF}_2\text{BrCl}$ (Halon 1211)	1.3	1.7
	$\text{CF}_3\text{CHFBr}$	1.0	1.7

The Table shows the extinguishment time 35 required for various fuels at 6.6% v/v of the agents employed. At this level, heptafluoropropane is as effective as bromine-containing Halons in extinguishing

- 9 -

an n-heptane flame and nearly effective as the other agents in extinguishing lighter fluid flames.

Levels of about 5-10% are preferred for general application of pure hydrofluorocarbons in accordance with this invention. The use of too little agent results in failure to extinguish the fire and can result in excessive smoke and probably release of HF due to combustion of the agent. The use of excessive amounts is wasteful and can lead to dilution of the oxygen level of the air to levels harmful to living things.

#### EXAMPLE 3

Example 1 was repeated with two white mice admitted to the chamber. After extinguishment, mice were exposed to combustion products for a total of 10 minutes before being removed from the chamber. All mice showed no ill effects during the exposure and appeared to behave normally after removal from the apparatus.

#### EXAMPLE 4

Dynamic burn test data for heptafluoropropane and 1,1,1,2,3,3-hexafluoropropane were obtained using the cup burner test procedure in which air and n-butane are continuously supplied to a flame produced in a glass cup burner. Vapor of the agent to be tested was mixed with air and introduced to the flame, with the concentration of agent being slowly increased until the flow was just sufficient to cause extinction of the flame. Data were obtained in this manner for heptafluoropropane and 1,1,1,2,3,3-hexafluoropropane and, for comparative purposes, for the following other Halon agents: Halon 1301 ( $\text{CF}_3\text{Br}$ ); Halon 1211 ( $\text{CF}_2\text{BrCl}$ ); Halon 251 ( $\text{CF}_3\text{CF}_2\text{Cl}$ ); Halon 25 ( $\text{CF}_3\text{CF}_2\text{H}$ ); and Halon 14 ( $\text{CF}_4$ ). The percent of each agent in air (v/v) required to extinguish the flame is given in Table 2.

- 10 -

TABLE 2

## Extinguishment of n-Butane Diffusion Flames

5	Air	Air flow	Agent Required	Agent In
	Agent % v/v	cc/min	cc/min	
10	Halon 1301 (CF <sub>3</sub> Br)	16,200	396	2.4
	Halon 1211 (CF <sub>2</sub> BrCl)	16,200	437	2.7
	Halon 251 (CF <sub>3</sub> CF <sub>2</sub> Cl)	16,200	963	5.9
15	CF <sub>3</sub> CHF CF <sub>3</sub>	16,200	976	6.0
	CF <sub>3</sub> CHF CHF <sub>2</sub>	16,200	1312	8.1
	Halon 25 (CF <sub>3</sub> CF <sub>2</sub> H)	16,200	1409	8.7
20	Halon 14 (CF <sub>4</sub> )	16,200	2291	14.1

EXAMPLE 5

Heptafluoropropane and Halon 1301, Halon 1211 25 and Halon 251 were used to extinguish n-heptane diffusion flames using the method of Example 4. Test data are reported in Table 3.

- 11 -

TABLE 3

## Extinguishment of n-Heptane Diffusion Flames

5	Air	Air flow	Agent Required	Agent In
	Agent % v/v	cc/min	cc/min	
10	Halon 1301 (CF <sub>3</sub> Br)	16,200	510	3.1
	Halon 1211 (CF <sub>2</sub> BrCl)	16,200	546	3.4
	Halon 251 (CF <sub>3</sub> CF <sub>2</sub> Cl)	16,200	1,006	6.2
15	CF <sub>3</sub> CHFCF <sub>3</sub>	16,200	1,033	6.4
	Halon 25 (CF <sub>3</sub> CF <sub>2</sub> H)	16,200	1,506	9.3

20           The dynamic test data reported in Tables 2 and 3 demonstrate that use of heptafluoropropane, 1,1,1,2,3,3-hexafluoropropane and pentafluoroethane in accordance with this invention is significantly more effective than other known non-bromine or chlorine

25 containing Halons such as Halon 14 (CF<sub>4</sub>). Moreover, heptafluoropropane is comparable in effectiveness to Halon 251, a chlorine containing chlorofluorocarbon. The latter relationship is shown with respect to n-heptane as well as n-butane fuels. While bromine and

30 chlorine-containing agents such as Halon 1301 and Halon 1211 are somewhat more effective than the hydrofluorocarbon agents under the cup burner test, the use of the agents in accordance with this invention remains highly effective and their use avoids the significant

35 environmental handicaps encountered with chlorine and bromine containing Halons such as Halon 1301, Halon 1211, and Halon 251.

- 12 -

EXAMPLE 6

Static box flame extinguishment data were obtained for 1,1,1,3,3,3-hexafluoropropane with a 35.2 litre test enclosure using the procedure of Example 1. In addition to 1,1,1,3,3,3-hexafluoropropane, for comparative purposes, Halon 1301, Halon 1211 and Halon 251 were also tested. All agents were delivered at a test concentration of 5.5% (v/v).

TABLE 4

10      Extinguishment Time (Seconds) for 5.5% (v/v) Agent

	<u>Agent</u>	<u>Extinction Time(s)</u>
	Halon 1301 (CF <sub>3</sub> Br)	1.02
15	Halon 1211 (CF <sub>2</sub> BrCl)	1.76
	Halon 251 (CF <sub>3</sub> CF <sub>2</sub> Cl)	2.15
	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	2.98
20		

The data of Table 4 demonstrates that 1,1,1,3,3,3-hexafluoropropane is a highly effective fire extinguishant. It is nearly as effective as Halon 251, a chlorofluorocarbon, and it is sufficiently effective, when compared to bromine containing Halons such as Halon 1301 and Halon 1211, that it is preferable by reason of the absence of ozone depletion and other environmental effects of the chlorine and bromine containing Halons.

30      In addition to being a highly effective agent for extinguishing fires, 1,1,1,3,3,3-hexafluoropropane at concentrations in accordance with the method of this invention is well within the range of toxicological safety.

35      The following Examples demonstrate the effective use of hydrofluorocarbon agents in accordance

- 13 -

with this invention in mixtures or blends including bromine-containing Halon fire extinguishants.

#### EXAMPLE 7

Dynamic test data using the cup burner procedure of Example 4 were obtained for various mixtures of heptafluoropropane and Halon 1201 ( $\text{CF}_2\text{HBr}$ ). Air and a mixture of the agents were continuously supplied to an n-heptane diffusion flame produced in a glass cup burner. For a given heptafluoropropane flow, the flow of  $\text{CF}_2\text{HBr}$  was slowly increased until the flow was just sufficient to cause extinction of the flame. The experiment was repeated at various heptafluoropropane flow rates, and the results are reported in Table 6.

Table 6 reports the actual volume percent in air as observed. Table 6 also reports the calculated weight percent heptafluoropropane in the mixture. In addition, Table 6 also reports the ozone depletion potential ("ODP") for each agent. ODP data for Halon 1201 was calculated in the following manner. ODP's for pure compounds were calculated by the following formula:

$$\text{ODP} = A E P [(\#Cl)^B + C(\#Br)] D^{(\#C-1)}$$

In this expression, P is the photolysis factor.  $P=1.0$  if there are no special structural features which make the molecule subject to tropospheric photolysis. Otherwise,  $P=F, G, \text{ or } H$ , as indicated in the table of constants, Table 5 below.

#### TABLE 5

CONSTANT	NAME	VALUE
F	Photolysis factor for geminal Br-C-Cl	0.180
30 G	Photolysis factor for geminal Br-C-Br	0.015
H	Photolysis factor for adjacent BR-C-C-Br	0.370
A	Normalizing constant	0.446
B	Exponent for chlorine term	0.740
C	Multiplier for bromine term	32.000
35 D	Constant for carbon term	1.120
E	Hydrogen factor [=1.0 for no H's]	.0625

- 14 -

ODP's for the mixtures were obtained by multiplying the weight percent of the Halon 1201 by the ODP of pure Halon 1201.

TABLE 6

5

## Extinguishment of n-Heptane Diffusion Flames

 $\text{CF}_3\text{CHF}\text{CF}_3$  /  $\text{CF}_2\text{HBr}$  Mixtures

	Flow at 10 Extinguishment cc/min		Volume % in Air		Total Vol %	Weight % $\text{CF}_3\text{CHF}\text{CF}_3$	ODP
	$\text{CF}_3\text{CHF}\text{CF}_3$	$\text{CF}_2\text{HBr}$	$\text{CF}_3\text{CHF}\text{CF}_3$	$\text{CF}_2\text{HBr}$			
15	0	1380	0	4.0	4.0	0	0.89
	164	489	1.0	3.0	4.0	30.1	0.62
	353	357	2.2	2.2	4.4	56.5	0.39
	533	216	3.3	1.3	4.6	76.6	0.21
	705	122	4.3	0.8	5.1	87.4	0.11
20	869	39	5.4	0.2	5.6	97.2	0.02
	1042	0	6.4	0	6.4	100.0	0.00

These data demonstrate that effective flame extinguishment may be obtained with mixtures of 25 heptafluoropropane and Halon 1201 and that the ODP of Halon 1201 can be materially reduced by providing heptafluoropropane therewith.



- 15 -

EXAMPLES 8-11

Tables 7, 8, 9 and 10 report diffusion flame extinguishment data obtained using the method of Example 7 for the following agent mixtures:

- 5                    Table 7 - heptafluoropropane and Halon 1211  
( $\text{CF}_2\text{BrCl}$ )
- Table 8 - heptafluoropropane and Halon 1301  
( $\text{CF}_3\text{Br}$ )
- Table 9 - pentafluoroethane and Halon 1201  
10 ( $\text{CF}_2\text{HBr}$ )
- Table 10- 1,1,1,2,3,3-hexafluoropropane and  
Halon 1201 ( $\text{CF}_2\text{HBr}$ )

These Tables also contain ODP data for pure Halons 1211 and 1301 as reported by the Lawrence  
15 Livermore Research Laboratories. ODP's for Halon 1201 were calculated using the method given above, and ODP's for the mixtures were obtained by multiplying the weight percent of the Halon agent by the ODP of the pure Halon.

TABLE 7

20

## Extinguishment of n-Heptane Diffusion Flames

 $\text{CF}_3\text{CHF}_3$  /  $\text{CF}_2\text{BrCl}$  Mixtures

	Flow at 25 Extinguishment cc/min		Volume % in Air		Total Vol %	Weight % $\text{CF}_3\text{CHF}_3$ ODP	
	$\text{CF}_3\text{CHF}_3$	$\text{CF}_2\text{BrCl}$	$\text{CF}_3\text{CHF}_3$	$\text{CF}_2\text{BrCl}$		$\text{CF}_3\text{CHF}_3$	ODP
30	0	546	0	3.4	3.4	0	2.64
	164	437	1.0	2.7	3.7	27.5	1.91
	262	378	1.6	2.3	3.9	41.7	1.54
	353	328	2.2	2.0	4.2	53.1	1.24
	533	210	3.3	1.3	4.6	72.5	0.73
35	705	109	4.3	0.7	5.0	86.3	0.36
	869	44	5.4	0.2	5.6	94.9	0.13
	1042	0	6.4	0	6.4	100.0	0.00

- 16 -

TABLE 8

Extinguishment of n-Heptane Diffusion Flames						
CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub> / CF <sub>3</sub> Br Mixtures						
5						
Flow at Extinguishment cc/min		Volume % in Air		Total	Weight %	ODP
10 CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub>	CF <sub>3</sub> Br	CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub>	CF <sub>3</sub> Br	Vol %	CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub>	
0	510	0	3.1	3.1	0	14.28
164	422	1.0	2.6	3.6	30.4	9.93
262	334	1.6	2.1	3.7	46.4	7.65
15 353	317	2.2	1.9	4.1	57.1	6.13
533	246	3.3	1.5	4.8	71.6	4.06
705	98	4.3	0.6	4.9	89.2	1.54
869	51	5.4	0.3	5.7	95.4	0.66
943	24	5.8	0.1	6.0	98.5	0.21
20 1042	0	6.4	0	6.4	100.0	0.00

- 17 -

TABLE 9

## Extinguishment of n-Heptane Diffusion Flames

 $\text{CF}_3\text{CF}_2\text{H}$  /  $\text{CF}_2\text{HBr}$  Mixtures

Flow at Extinguishment cc/min		Volume % in Air		Total Vol %	Weight % $\text{CF}_3\text{CF}_2\text{H}$	ODP
10 $\text{CF}_3\text{CF}_2\text{H}$	$\text{CF}_2\text{HBr}$	$\text{CF}_3\text{CF}_2\text{H}$	$\text{CF}_2\text{HBr}$			
0	1380	0	4.0	4.0	0	0.89
196	526	1.2	3.2	4.4	25.6	0.66
314	470	1.9	2.9	4.8	37.5	0.56
15 421	423	2.6	2.6	5.2	47.7	0.46
637	338	3.9	2.1	6.0	63.0	0.33
1039	109	6.4	0.7	7.1	89.4	0.09
1509	0	9.3	0	9.3	100.0	0.00

20

TABLE 10

## Extinguishment of n-Heptane Diffusion Flames

 $\text{CF}_3\text{CHF}\text{CF}_2\text{H}$  /  $\text{CF}_2\text{HBr}$  Mixtures

Flow at Extinguishment cc/min		Volume % in Air		Total Vol %	Weight % $\text{CF}_3\text{CHF}\text{CF}_2\text{H}$	ODP
25 $\text{CF}_3\text{CHF}\text{CF}_2\text{H}$	$\text{CF}_2\text{HBr}$	$\text{CF}_3\text{CHF}\text{CF}_2\text{H}$	$\text{CF}_2\text{HBr}$			
0	1380	0	4.0	4.0	0	0.89
196	508	1.2	3.1	4.3	30.8	0.62
421	423	2.6	2.6	5.2	53.7	0.41
637	367	3.9	2.3	6.2	66.3	0.30
35 843	207	5.2	1.3	6.5	82.1	0.16

- 18 -

The data of Tables 7 through 10 demonstrate that various mixtures of hydrofluorocarbons in accordance with this invention with chlorine and/or bromine-containing Halons are effective flame extinguishment agents and that significant reductions in ODP of the chlorine and/or bromine containing materials can be obtained by admixture thereof with hydrofluorocarbons in accordance with this invention. Saturated higher fluorinated C<sub>2</sub> and C<sub>3</sub> hydrofluorocarbons such as heptafluoropropane, 1,1,1,2,3,3-hexafluoropropane, 1,1,1,3,3,3-hexafluoropropane and pentafluoroethane, like the presently employed chlorine and bromine-containing Halons, are nondestructive agents, and are especially useful where cleanup of other media poses a problem. Some of the applications of the hydrofluorocarbons of this invention are the extinguishing of liquid and gaseous fueled fires, the protection of electrical equipment, ordinary combustibles such as wood, paper and textiles, hazardous solids, and the protection of computer facilities, data processing equipment and control rooms.

- 19 -

CLAIMS

1. A method for extinguishing a fire comprising the steps of introducing to the fire a fire extinguishing concentration of one or more compounds of the formula  $C_xH_yF_z$ , where x is 2 or 3, y is 1 or 2, and z is 5, 6 or 7; where y is 1 and z is 5 when x is 2; and where z is 6 or 7 when x is 3, and maintaining the concentration of the compound until the fire is extinguished.
- 10 2. A process, as claimed in claim 1, wherein the compound is employed at a level of less than about 15% (v/v).
3. A process, as claimed in Claim 1, wherein the extinguishing concentration of the compound is from 15 about 5 to 10% (v/v).
4. A process, as claimed in Claim 1, wherein the compound is employed in a total flooding system.
5. A process, as claimed in Claim 1, wherein the compound is employed in a portable extinguishing  
20 system.
6. The use of one or more compounds of the formula  $C_xH_yF_z$ , where x is 2 or 3, y is 1 or 2, and z is 5, 6 or 7; where y is 1 and z is 5 when x is 2; and where z is 6 or 7 when x is 3, as a nondestructive fire  
25 extinguishing agent.
7. A process, as claimed in claim 1, wherein the compound is a member selected from the group consisting of heptafluoropropane, 1,1,1,3,3,3-hexafluoropropane, 1,1,1,2,3,3-hexafluoro-  
30 propane, pentafluoroethane, and mixtures thereof.
8. A process, as claimed in any of claims 1 to 7, wherein the compound is heptafluoropropane.
9. A process for extinguishing a fire comprising the steps of introducing heptafluoropropane at  
35 a concentration of about 5 to 15 % (v/v) to the fire and maintaining the concentration of heptafluoropropane until the fire is extinguished.

- 20 -

10. A method for extinguishing a fire comprising the steps of:

introducing to the fire a fire extinguishing concentration of a mixture comprising:

5 one or more compounds of the formula  $C_xH_yF_z$ , where x is 2 or 3, y is 1 or 2, and z is 5, 6 or 7; where y is 1 and z is 5 when x is 2; and where z is 6 or 7 when x is 3; and

one or more chlorine and/or bromine containing  
10 fire extinguishing agent selected from the group consisting of  $CF_3Br$ ,  $CF_2BrCl$ ,  $CF_3CF_2Cl$ ,  $CF_2BrCF_2Br$ ,  $CF_2HBr$  and  $CF_3CHFBr$ ,

wherein the compound is present in the mixture at a level of at least about 10% by weight of the  
15 mixture; and

maintaining the concentration of the mixture until the fire is extinguished.

11. A method, as claimed in claim 10, wherein the fire extinguishing concentration of the mixture is  
20 about 3 to 15% (v/v).

12. A fire extinguishing mixture comprising:  
at least about 10%, by weight of the mixture, of one or more compounds of the formula  $C_xH_yF_z$ , where x is 2 or 3, y is 1 or 2, and z is 5, 6 or 7; where y is 1 and z is 5  
25 when x is 2; and where z is 6 or 7 when x is 3; and

no more than about 90%, by weight of the mixture, of one or more chlorine and/or bromine containing fire extinguishing agents selected from the group consisting of  $CF_3Br$ ,  $CF_2BrCl$ ,  $CF_3CF_2Cl$ ,  $CF_2BrCF_2Br$ ,  
30  $CF_2HBr$  and  $CF_3CHFBr$ .

13. A fire extinguishing mixture, as claimed in claim 12, wherein the compound is heptafluoropropane and the member is  $CF_2HBr$ .

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US90/04467

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.(5): A62C 3/00

US CL.: 169/46

## II. FIELDS SEARCHED

Minimum Documentation Searched \*

Classification System

Classification Symbols

US 169/44, 46, 47, 11, 54, 30, 49; 252/2, 3, 8, 8.05

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*\*

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
X	US, A, 4,459,213 UCHIDA et al., 10 July 1984 See the abstract and column 2, lines 40-58.	1,6,7,10,12
X	US, A, 4,830,762 YAMAGUCHI et al., 16 May 1989 See column 4, lines 20-33.	1,6,7
X	US, A, 4,954,271 GREEN 04 September 1990 See the abstract.	1,6,7
X	JP, A, 51-34,595 DAIKIN KOGYO KK 24 March 1976 See the English abstract.	1,6,7,10,12

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"G" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search \*

16 OCTOBER 1990

International Searching Authority \*

ISA/US

Date of Mailing of this International Search Report \*

06 FEB 1991

Signature of Authorized Officer to

JAMES M. KANNOFSKY

K(19)

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Стр. 2, строки 17 - 24

Хотя упомянутые бромированные галлоны являются эффективными пламягасящими веществами, но некоторые считают, что вещества, содержащие бром или хлор имеют, свойство разрушать защитный озоновый слой Земли. При этом, поскольку эти вещества не содержат атомов водорода, которые обеспечили возможность их разрушения в тропосфере, эти вещества также могут вносить свой вклад в создание «парникового эффекта».